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Kinetic Zr isotope fractionation on Mars recorded in ancient Zr-rich minerals

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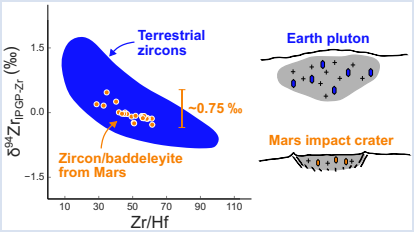
Abstract



Zircon crystallisation induces stable Zr isotope fractionation by the preferential incorporation of the lighter Zr isotopes. The Zr isotope compositions recorded in terrestrial zircons show that, in most cases, the magnitude of isotope fractionation exceeds that expected from thermodynamic equilibrium. In other words, kinetic Zr isotope fractionation between zircon and silicate melt is the rule rather than the exception. Here, we investigate the stable Zr isotope compositions of ~4.45 Gyr-old zircon and baddeleyite grains from the meteorite Northwest Africa (NWA) 7533, a regolith breccia sample from Mars. These Zr-rich minerals crystallised during impact reworking of the primordial Martian crust and, thus, probe a magmatic system fundamentally different from the plutons and batholiths represented in the existing zircon Zr isotope data. The 26 analysed grains reveal a total $^{94}Zr/^{90}Zr$ variation of ~0.75 ‰, indicative of kinetic isotope fractionation. Further, the grains record a correlation between $^{94}Zr/^{90}Zr$ and Zr/Hf, similar to that observed in terrestrial zircon samples, suggesting that the fractionation behaviour in Pre-Noachian impact melt systems on Mars is similar to that occurring in younger magmatic intrusions on Earth.

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Introduction

Zirconium is a high field strength element with five naturally occurring stable isotopes (^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr). Since the first demonstrations of stable Zr isotope analysis by isotope dilution multi-collector inductively coupled mass spectrometry (MC-ICPMS; Inglis *et al.*, 2018) and laser-ablation MC-ICPMS analysis of zircon (Zhang *et al.*, 2019), several subsequent studies have documented mass dependent stable Zr isotope fractionation in nature (*e.g.*, Inglis *et al.*, 2019; Guo *et al.*, 2020; Tian *et al.*, 2021; Yuan *et al.*, 2022). As a result, abundant Zr isotopic data exist for zircons from a wide range of felsic lithologies (granites, granitoids and pegmatite; *e.g.*, Zhu *et al.*, 2024; Li *et al.*, 2025) and a few mafic lithologies (gabbro and troctolite; *e.g.*, Ma *et al.*, 2025). This extensive dataset shows that, in most silicate–magmatic settings, zircon preferentially incorporates lighter Zr isotopes, consistent with first-principles predictions of mass dependent isotope fractionation between zircon and silicate melt at thermodynamic equilibrium (Chen *et al.*, 2020; Méheut *et al.*, 2021). This behaviour is theoretically explained by the preference of heavier isotopes for the shorter and stiffer bonds that characterise the low coordination configurations of Zr in the silicate melt relative to zircon (Bigeleisen and Mayer, 1947; Urey, 1947; Chen *et al.*, 2020). Thus, progressive zircon crystallisation generally enriches the residual melt in heavier Zr isotopes, leading to heavier Zr isotopic compositions in later formed crystals. Due to the preferential incorporation of Zr over Hf in zircon (Claiborne *et al.*, 2006), this enrichment in heavy Zr isotopes in the residual melt is accompanied by a decreasing Zr/Hf ratio as crystallisation progresses, leading to a negative correlation between $^{94}Zr/^{90}Zr$ and Zr/Hf. Indeed, most zircon literature data exhibit a negative correlation between $\delta^{94}Zr$ (the per mil deviation of the $^{94}Zr/^{90}Zr$ ratio in the sample relative to the reference material) and Zr/Hf, with lower $\delta^{94}Zr$ and higher Zr/Hf ratios indicative of earlier crystallisation (*e.g.*, Guo *et al.*, 2020; Yuan *et al.*, 2023; Zhu *et al.*, 2023). However, the magnitude of stable Zr isotope fractionation recorded in zircon typically exceeds that expected from equilibrium fractionation, reflecting an additional isotope fractionation mechanism. Such a mechanism has been proposed to be diffusion-driven (kinetic) Zr isotope fractionation, which describes the isotope fractionation that occurs due to Zr diffusion in the melt (in response to Zr concentration gradients) and the faster diffusion of lighter relative to heavier Zr isotopes (Chen *et al.*, 2020; Méheut *et al.*, 2021). As this process can readily induce Zr isotope fractionation at the per mil level, a general consensus has been established that the stable Zr isotope variations in natural zircon results from a combination of equilibrium and diffusion-driven kinetic isotope fractionation (*e.g.*, Guo *et al.*, 2023). Nonetheless, the factors controlling the relative roles of diffusion and equilibrium fractionation in silicate melt systems remain unclear, and further work is needed to constrain the extent of disequilibrium fractionation generated during different crust formation processes. In fact, it may be informative to study the stable Zr isotope compositions of zircons formed in the early history of planetary bodies where crust formation was partially controlled by impact melting and, thus, fundamentally different from later times (*e.g.*, Johnson *et al.*, 2018). The Martian polymict regolith breccia meteorite Northwest Africa (NWA) 7034 and paired stones (*e.g.*, NWA

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7533) contain zircon and baddeleyite with ages up to ~4480 Ma that formed from impact reworking of the primordial Martian crust (Bouvier *et al.*, 2018; Costa *et al.*, 2020). These samples, therefore, provide a unique opportunity to investigate Zr isotope fractionation under early planetary conditions. We emphasise that the predicted equilibrium Zr isotope fractionation between baddeleyite and silicate melt is of similar magnitude to that calculated for zircon and, as such, we expect a similar isotope fractionation behaviour for these two Zr-rich minerals (Chen *et al.*, 2020).

This study presents the first stable Zr isotope data for zircon and baddeleyite from Mars that formed within the early history of the planet during crustal reworking. We show that ~4.45 Gyr-old zircon and baddeleyite grains from NWA 7533 typically record isotopically light Zr isotope compositions relative to the presumed parent melt composition, with a fractionation magnitude suggesting kinetic isotope fractionation effects.

Methods

We conducted U-Pb, Lu-Hf, and stable Zr isotope measurements for 26 zircon and baddeleyite grains separated from the Martian polymict regolith breccia meteorite NWA 7533 following established procedures (Costa *et al.*, 2020; Jensen *et al.*, 2024). In detail, 17 zircons and four baddeleyites derive from a crushed bulk aliquot of the meteorite, and five zircons were separated from a basaltic andesitic clast ("C28"; Jensen *et al.*, 2025b). Most of the zircons used in this study had a brown and granular appearance, indicating metamictisation (Figs. S-1 to S-3). Whereas disturbed U-Pb isotope systematics are expected, these metamict grains might preserve pristine Lu-Hf and Zr isotope compositions (see SI for further details). We highlight that an assessment of the degree of isotope disturbance is permitted in this study through the concomitant determination of the U-Pb, Lu-Hf and stable Zr isotope compositions of the grains. In brief, the U-Pb isotope analyses were conducted by isotope dilution thermal ionisation mass spectrometry (ID-TIMS), and the Lu-Hf (unspiked) and Zr double-spiked isotope analyses were conducted by solution-based MC-ICPMS. We stress that the individual zircon and baddeleyite crystals were processed as single grains, and the presented isotope and trace element data reflect the same grain volume. To allow for a comparison to terrestrial zircon data, the stable Zr isotope compositions are corrected for the mass independent ^{96}Zr enrichment of Mars relative to Earth (see Supplementary Information for details), and the results are reported relative to the IPGP-Zr reference material as:

$$\delta^{94}\mathrm{Zr}\,[‰] = \left[\frac{(^{94}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{sample}}}{(^{94}\mathrm{Zr}/^{90}\mathrm{Zr})_{\mathrm{IPGP-Zr}}} - 1\right] \times 10^3 \qquad \text{Eq. 1}$$

U-Pb and Lu-Hf Isotope Results

In accordance with the metamict appearance of the majority of the grains investigated in this study, only five out of 26 grains yield concordant U-Pb ages (Table S-3). While zircon NS5b5 yields the oldest age with a ^{207}Pb/^{206}Pb date of 4479.8 ± 1.9 Ma (2 s.e.), the four investigated baddeleyite grains record a ~200 Myr age range from ~4255 to ~4470 Ma. The remaining 21 grains exhibit U-Pb age discordances between 5 % and 50 %, defining an array with approximate upper and lower concordia line intercepts at 4.45 Ga and 1.4 Ga (Fig. S-4). This is consistent with the results of previous studies of NWA 7034/7533 minerals, suggesting that the meteorite source region experienced a thermal event at 1.3–1.7 Ga (*e.g.*, Humayun *et al.*, 2013; Bellucci *et al.*, 2015; McCubbin *et al.*, 2016; Cassata *et al.*, 2018).

The five concordant grains return initial epsilon Hf values (εHf, the ^{176}Hf/^{177}Hf composition of the sample relative to that of the CHondritic Uniform Reservoir) between 0 and −4, with the more negative values corresponding to the younger grains. While the highly discordant grains have experienced significant Pb loss at ~1.4 Ga, the Lu-Hf isotope systematics are undisturbed with ^{176}Lu/^{177}Hf and ^{176}Hf/^{177}Hf ratios that follow the isotopic trend defined by concordant zircon and baddeleyite samples from NWA 7034/7533 (Fig. S-9), with the exception of one grain with a relatively radiogenic Hf isotope composition (NS5b6; see SI for further details). Thus, we can confirm that the investigated grains belong to the population of ~4.45 Gyr-old crystals from NWA 7533 that formed during reworking of the primordial Martian crust.

Stable Zr Isotope Results

The 26 grains record stable Zr isotope fractionation with $\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ compositions ranging from −0.281 ± 0.011 ‰ in the concordant zircon NS5b5 to +0.468 ± 0.009 ‰ in the baddeleyite NS4b1 (Fig. 1, Table S-3). Notably, 22 of the grains exhibit $\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ values lower than the Martian mantle value ($\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ = 0.062 ± 0.043 ‰; Jensen *et al.*, 2025a), and three out of four baddeleyites record $\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ values heavier than the mantle. The zircons from clast C28 form two groups, with the two largest zircons yielding $\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ of about −0.250 ‰, and the three smaller grains yielding $\delta^{94}\mathrm{Zr}_{\mathrm{IPGP\text{-}Zr}}$ close to 0 ‰. Importantly, the stable Zr isotope compositions do not correlate

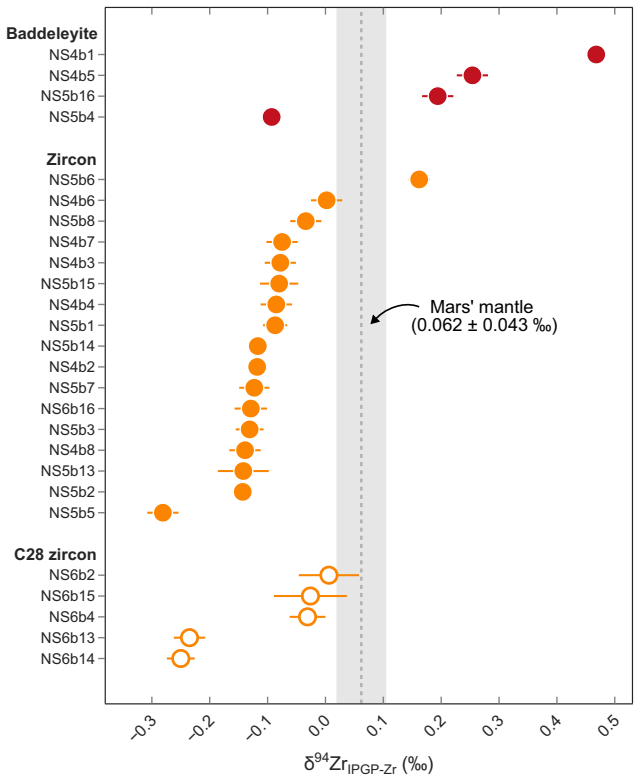

Figure 1 Stable Zr isotope results for zircon and baddeleyite from NWA 7533. The grey dotted line and shaded bar reflect the stable Zr isotope composition inferred for the Martian mantle (Jensen *et al.*, 2025a). The data point error bars reflect the 2-standard error of the mean.

with the degree of U-Pb age discordance (Fig. S-6a), reflecting that the Zr isotopes were, in general, not affected during the ~1.4 Ga event that led to partial U-Pb isotope resetting, in agreement with the preservation of undisturbed Lu-Hf isotope systematics. However, the zircon with an anomalously radiogenic Hf isotope signature (NS5b6) records a heavier stable Zr isotope composition ($\delta^{94}Zr_{IPGP\text{-}Zr} = 0.162 \pm 0.010$ ‰) relative to the other zircons. This may reflect partial recrystallisation during the ~1.4 Ga thermal event, consistent with the almost complete resetting of the U-Pb isotope systematics in this grain (Table S-3, Fig. S-4).

Comparison to Terrestrial Zircons

The stable Zr isotope compositions of the NWA 7533 grains exhibit a negative correlation with the Zr/Hf ratios, similar to the trends observed for most terrestrial zircon datasets (Fig. 2). This illustrates the typical evolution of the magma towards a heavier Zr isotope composition due to fractional crystallisation of zircon and/or baddeleyite. The zircon and baddeleyite grains from Mars investigated here have $\delta^{94}Zr$ compositions at the lighter end of the correlation defined by zircons from terrestrial rocks with $SiO_2 > 65$ wt. % and MgO < 2 wt. % (Fig. 2a,b). This may reflect the origin of the NWA 7533 grains from less evolved melts, which is consistent with the typically basaltic composition of igneous clasts from the NWA 7533 breccia meteorite (*e.g.*, Santos *et al.*, 2015; Jensen *et al.*, 2025b).

The lower compositional variability in the NWA 7533 grains compared to terrestrial zircon data may partly reflect methodological differences. This study probes the bulk grain compositions (full dissolution method) while terrestrial zircon data typically reflects laser ablation MC-ICPMS, which captures both inter- and intra-grain variability. As zircon intra-grain $\delta^{94}Zr$ variability can be at the per mil level (up to 2.8 ‰ in Haladala pluton zircon; Ma *et al.*, 2025), a lower degree of Zr isotope variability may be expected in the zircon data presented here relative to the compiled terrestrial zircon dataset. Despite this, the NWA 7533 bulk grains exhibit $\delta^{94}Zr$ and Zr/Hf variations comparable to the inter-/intra-grain variability observed for zircons from the Taihua Complex and the Linglong granite batholith in the North China Craton and the Barberton Granitoid-Greenstone Terrane in the Kaapvaal Craton (Fig. S-10; Zhu *et al.*, 2023; Li *et al.*, 2025).

Kinetic Zr Isotope Fractionation

The total $\delta^{94}Zr$ range of ~0.75 ‰ exhibited by the 26 investigated grains reveals that the early reworking of the primordial Martian crust was associated with stable Zr isotope fractionation, similar to that occurring in plutons and batholiths on Earth. Given that the investigated grains were extracted from a polymict regolith breccia, they may plausibly derive from different rock fragments and record the crystallisation of different magmatic source reservoirs. However, we emphasise that the $^{176}Hf/^{177}Hf$-$^{176}Lu/^{177}Hf$ correlation exhibited by the grains (Fig. S-9) indicates that their magmatic source(s) can be treated as a single closed system that evolved from the same initial $^{176}Hf/^{177}Hf$ isotope composition. If new magma was introduced to this system in the time frame of zircon/baddeleyite crystallisation, it must have been relatively depleted in Hf (and other incompatible trace elements such as Zr) to preserve undisturbed Lu-Hf isotope systematics. Consequently, the Zr isotope compositions of the grains most likely reflect closed-system evolution from a uniform initial $\delta^{94}Zr$. Moreover, it is reasonable to assume that the evolution of the Zr isotope composition of the system is dominantly controlled by zircon/baddeleyite fractional crystallisation rather than by primary rock-forming minerals, such as pyroxene, based on the limited stable Zr isotope fractionation recorded in bulk clasts from NWA 7533 (Jensen *et al.*, 2025a). We therefore model the stable Zr isotope and Zr/Hf evolution of the system as a function of zircon/baddeleyite fractional crystallisation (Rayleigh fractionation). Assuming the initial melt had a Martian mantle $\delta^{94}Zr_{IPGP\text{-}Zr}$ composition ($\delta^{94}Zr_{IPGP\text{-}Zr} = 0.062 \pm 0.043$ ‰; Jensen *et al.*, 2025a) and an initial Zr/Hf ratio of 39 (the composition of the bulk NWA 7533 breccia; Jensen *et al.*, 2025b), we find that the $\delta^{94}Zr$ compositional range of the NWA 7533 grains cannot be reproduced by equilibrium Zr isotope fractionation alone (Fig. 3). This conclusion holds even when constraints on the initial melt composition are relaxed. For example, assuming a significantly lighter initial melt $\delta^{94}Zr_{IPGP\text{-}Zr}$ composition (−0.07 ‰) and higher Zr/Hf ratio (51) still fails to fully explain the compositional range of the NWA 7533 grains through equilibrium isotope fractionation alone (Fig. S-13).

Instead, the Zr isotope fractionation preserved in the Martian grains must partly reflect a kinetic process, such as diffusion-limited crystallisation (*e.g.*, Chen *et al.*, 2020). Using a mineral-melt Zr/Hf fractionation factor (Kd^{Zr}/Kd^{Hf}) of 2 (the predicted value for equilibrium fractionation at 700 °C), a fraction of

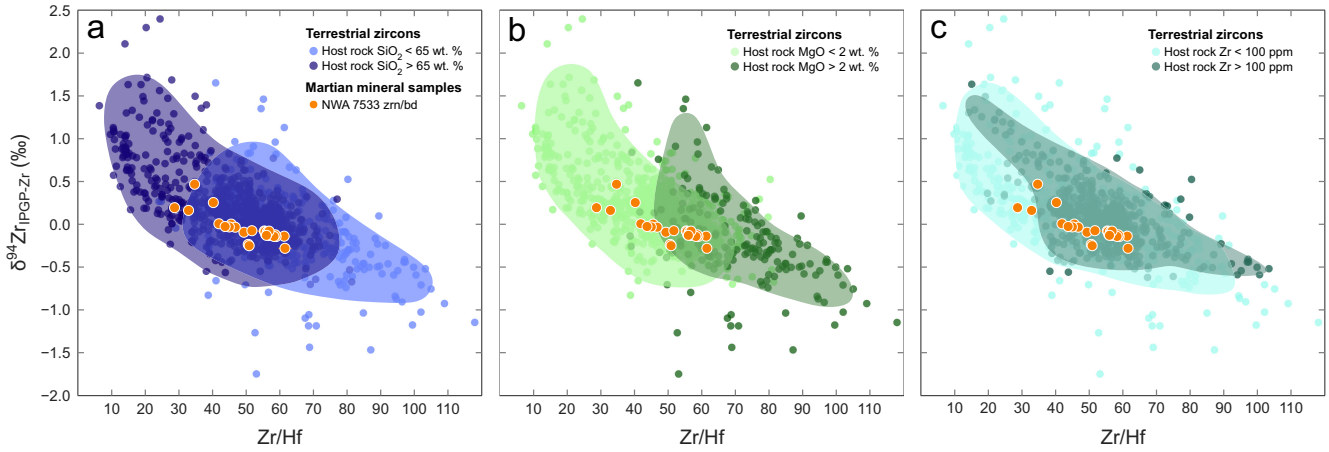

Figure 2 Both NWA 7533 samples and terrestrial zircons show a negative correlation between $\delta^{94}Zr$ and Zr/Hf. Zircons from high-SiO_2, low-MgO host rocks trend toward heavier $\delta^{94}Zr$ and lower Zr/Hf values. Terrestrial zircon data are from Ibañez-Mejia and Tissot (2019), Yuan *et al.* (2023), Z. Zhu *et al.* (2023), E.-L. Zhu *et al.* (2024), Li *et al.* (2025), Ma *et al.* (2025), and Wang *et al.* (2025).

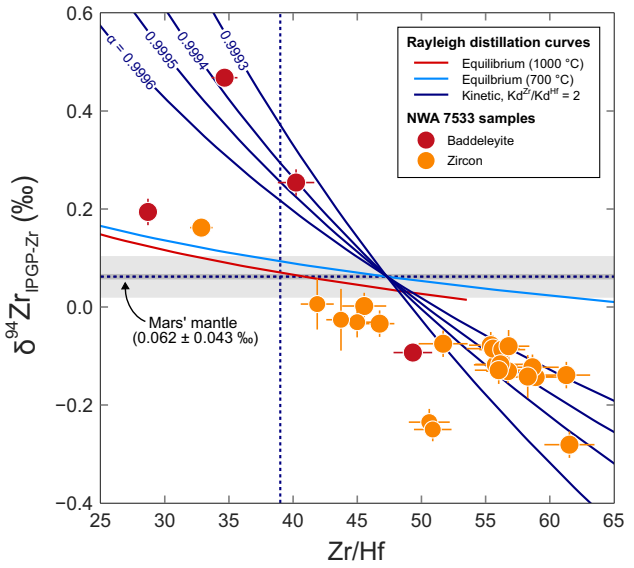

Figure 3 The δ^{94}Zr and Zr/Hf compositions of NWA 7533 zircon and baddeleyite are plotted with Rayleigh fractionation curves for equilibrium isotope fractionation at 1000 °C ($\alpha = 0.99995$, $Kd^{Zr}/Kd^{Hf} = 1.4$) and 700 °C ($\alpha = 0.99992$, $Kd^{Zr}/Kd^{Hf} = 2.0$), and kinetic isotope fractionation ($Kd^{Zr}/Kd^{Hf} = 2$, $\alpha = 0.9993$ to 0.9996). Dotted lines show the assumed initial melt composition, where $\delta^{94}Zr_{IPGP\text{-}Zr}$ represents the Martian mantle composition (0.062 ± 0.043 ‰; Jensen *et al.*, 2025a), and Zr/Hf = 39 represents bulk NWA 7533 (Jensen *et al.*, 2025b). The shaded grey field shows uncertainty in the Martian mantle composition.

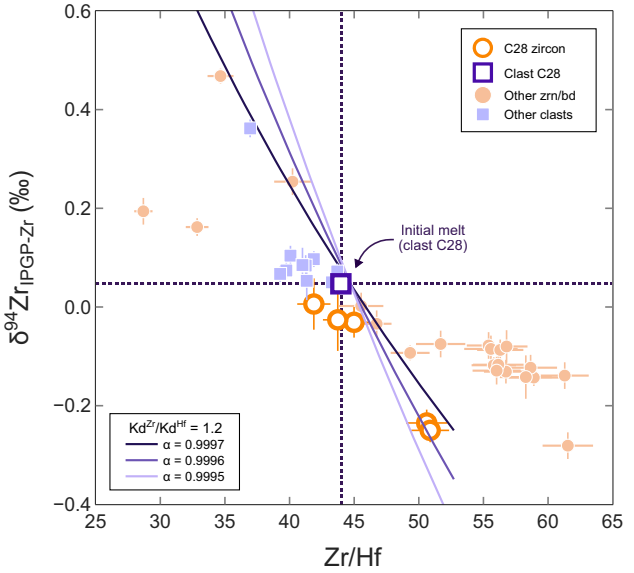

Figure 4 Rayleigh fractionation models assuming an initial melt composition akin to the host clast (the dotted lines). The three curves correspond to $Kd^{Zr}/Kd^{Hf} = 1.2$, but variable α. These models cannot explain the three smaller C28 zircons which have heavier Zr isotope compositions. The NWA 7533 clast data is from Jensen *et al.* (2025a, 2025b).

the NWA 7533 grains can be matched by Rayleigh fractionation with α values ranging from 0.9993 to 0.9996, reflecting a mixture of equilibrium and kinetic isotope fractionation processes (Fig. 3). These isotope fractionation factors are similar to those inferred from terrestrial zircons from different granitic bodies (*e.g.*, Guo *et al.*, 2020; Zhu *et al.*, 2023). Thus, we find that the stable Zr isotope fractionation occurring during crustal reworking on early Mars is partly kinetic in origin and similar in magnitude to that occurring in many terrestrial silicate systems. Since the magnitude of generated kinetic isotope fractionation reflects the net effect of several melt conditions (*e.g.*, cooling, mineral growth and element diffusion rates), it is unclear to what extent the conditions in early Martian impact melts were similar to those in terrestrial magma intrusions. However, we can conclude that stable Zr isotope fractionation of comparable magnitude occurs in different tectonic settings: intrusive silicate melt systems on Earth and impact melt bodies on Mars. Further work is required to determine whether the magnitude of kinetic stable Zr isotope fractionation in zircon is unambiguously linked to specific melt conditions such as cooling rate, which will determine the utility of the stable Zr isotope system as a tracer for magmatic processes.

Complex Zr Isotope Fractionation Systematics Recorded in Clast C28 Zircons

Whereas the petrological context is unknown for most of the grains investigated in this study, five zircons derive from the basaltic andesitic clast C28, providing additional constraints on the zircon parental melt composition. Notably, Rayleigh fractionation curves that assume an initial melt composition akin to the bulk C28 clast (with $\alpha = 0.9995$ to 0.9997, $Kd^{Zr}/Kd^{Hf} = 1.2$) approach the compositions of the two largest C28 zircons (NS6b13 and NS6b14, Fig. 4). However, the three smaller zircons with heavier δ^{94}Zr require fractionation factors closer to equilibrium and only minor Zr/Hf fractionation. Thus, the stable Zr isotope compositions of the five zircons from clast C28 cannot be explained by a single Rayleigh fractionation model (Fig. 4). Instead, a range of α and Kd^{Zr}/Kd^{Hf} values is required to explain the zircon compositions if the initial melt was identical to the host clast. Given the nearly basaltic composition of C28, the crystallisation of the C28 zircons likely took place in late-stage melt pockets, and the governing Zr/Hf and δ^{94}Zr fractionation factors may reflect the variable effects of co-crystallising phases on the element concentration gradients in these melt pockets.

Alternatively, the zircons could have formed from a parental melt composition distinct from that of the bulk clast. For example, the measured clast composition may not be representative for the true bulk rock, or the clast could represent a cumulate (Fig. S-11). However, the limited number of separated zircons from this clast and the very small size of most of these grains prevent us from constraining the formation history further. Nonetheless, the results support a model in which the Zr isotope fractionation recorded in the C28 zircons was partly controlled by a kinetic process. This is consistent with the observations from the NWA 7533 zircon and baddeleyite grains without petrological context.

To conclude, we find that stable Zr isotope fractionation associated with crustal reworking on early Mars was partly kinetic in nature. Moreover, the δ^{94}Zr and Zr/Hf fractionation recorded in the ancient Martian grains from mafic impact melt environments is similar to that observed for zircons from terrestrial magmatic intrusions. Further investigations of intra-grain Zr isotope fractionation in NWA 7533 zircons are required for direct comparison of the magnitudes of kinetic Zr isotope fractionation occurring in terrestrial plutons and Pre-Noachian impact melt systems on Mars.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2604.

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